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# PATENT ABSTRACTS OF JAPAN

(11)Publication number : **10-067894**
(43)Date of publication of application : **10.03.1998**

(51)Int.CI. **C08L 23/10**
**A61L 29/00**
**A61L 31/00**
**C08L 53/02**

(21)Application number : **09-148532**
(22)Date of filing : **22.05.1997**

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(30)Priority
Priority number : **08151717** Priority date : **23.05.1996** Priority country : **JP**

## (54) RESIN COMPOSITION AND MEDICAL SUPPLIES PRODUCED THEREFROM

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain a resin compsn. which gives a molded item excellent in softness, clarity, heat resistance, and blood compatibility by compounding a polyopropylene resin with a specific hydrogenated block copolymer.
SOLUTION: This compsn. comprises 10-90wt.% polypropylene resin having a melt flow rate of 0.1-500 and 90-10wt.% hydrogenated block copolymer which contains at least one polymer block A formed from an arom. vinyl compd. and at least one polyisoprene block Bhaving a content of 1,2- and 3,4-bonds of 10-75mol% and has a content of arom. vinyl compd. units of 10-40wt.% and a degree of hydrogenation of carbon-carbon double bonds of block B of 70% or higher or which contains at least one polymer block A and at least one polymer block C formed from a mixture of isoprene and butadiene in a vrt. ratio of (5/95)-(95/5) and having a content of 1,2- and 3,4-bonds of 20-85mol% and has a content of arom. vinyl compd. units of 10-40wt.% and a degree of hydrogenation of carbon-carbon double bonds of block C of 70% or higher.

cln 8

LEGAL STATUS

[Date of request for examination] 24.03.2003
[Date of sending the examiner's decision of rejection]
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]
[Date of final disposal for application]
[Patent number]
[Date of registration]
[Number of appeal against examiner's decision of rejection]
[Date of requesting appeal against examiner's decision of rejection]
[Date of extinction of right]

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention is excellent in flexibility and transparency, and relates to the medical supply which consists of the resin constituent and this constituent which are used suitable for especially a medical-application way.

[0002]

[Description of the Prior Art] Since to excel in flexibility and transparency is demanded, medical supplies, such as a catheter, blood circuits, and a blood bag, are manufactured in many cases using the elasticity vinyl chloride which is the material which has the property of these both. However, the elasticity vinyl chloride is added comparatively so much [ the plasticizer of low molecular weight, such as DOP (dioctyl phthalate) ], and the problem of elution of a plasticizer is pointed out from the field of safety. Moreover, although disposable-ization of a medical supply is advanced and it is destroyed more often by fire after use in recent years, the medical supply which used the elasticity vinyl chloride generates poisonous gas in the case of incineration, and has the problem of becoming the cause of environmental pollution.

[0003] Moreover, although sterilization is generally performed using ethylene oxide gas (ethylene oxide gas), as for the medical supply made from an elasticity vinyl chloride, we are anxious about the bad influence to the patient by Remains ethylene oxide gas. Although it is possible to switch to the autoclave sterilization (autoclave sterilization) which is other sterilization in order to lose the influence of Remains ethylene oxide gas, an elasticity vinyl chloride has bad thermal resistance, and cannot bear this sterilization.

[0004] For this reason, recently, replacing an elasticity vinyl chloride to other materials as a material of a medical supply is examined, it excels in flexibility, and the resin constituent which consists of an olefin system resin, a hydrogenation object of a styrene-butadiene block copolymer, and a hydrogenation object of a styrene-isoprene block copolymer is proposed by JP,4-159344,A as a resin constituent which gives the moldings suitable for medical application.

[0005]

[Problem(s) to be Solved by the Invention] The resin constituent indicated by above-mentioned JP,4-159344,A gives the moldings excellent in flexibility, and has the feature of not being accompanied by generating of poisonous gas even if it moreover incinerates a moldings. However, the moldings obtained from this resin constituent cannot be enough satisfied in another property demanded in a medical supply, i.e., transparency, and the room of improvement is accepted in this point. A deer is carried out, and when this invention gives the moldings excellent in flexibility and transparency and you moreover destroy by fire, let it be a technical problem to offer the resin constituent which gives the medical supply which is not made to generate poisonous gas, is enough also as for thermal resistance and is equal to autoclave sterilization.

[0006]

[Means for Solving the Problem] According to this invention, the above-mentioned technical problem the polymer block A which serves as a polypropylene regin (a) from a vinyl (b-1) aromatic compound One or more pieces, And the content of 1 and 2-combination and 3 and 4-combination has one or more 10-75-mol blocks [ polyisoprene ] B it is [ blocks ] %. The hydrogenation block copolymer which the content of a vinyl aromatic compound is 10 - 40 % of the weight, and comes to hydrogenate 70% or more of the carbon-carbon double bond of the polyisoprene block B, The polymer block A which consists of a vinyl aromatic compound One or more pieces, (b-2) And it consists of a polymer of the mixture which comes to mix an isoprene and a butadiene by the weight ratio of 5 / 95 - 95/5. The content of 1 and 2-combination and 3 and 4-combination has one or more 20-85-mol blocks [ polymer ] C it is [ blocks ] %. The hydrogenation block copolymer which the content of a vinyl aromatic compound is 10 - 40 % of the weight, and comes to hydrogenate 70% or more of the carbon-carbon double bond of the polymer block C, The polymer block A which consists of a vinyl aromatic compound And (b-3) one or more pieces, And it has one or more polybutadiene blocks D whose contents of 1 and 2-combination are more than 45 mol %. It consists of at least one sort of hydrogenation block copolymers (b) chosen from the group which consists of a hydrogenation block copolymer which the content of a vinyl aromatic compound is 10 - 40 % of the weight, and comes to hydrogenate 70% or more of the carbon-carbon double bond of the polybutadiene block D. It is solved by offering the resin constituent whose rates of both are polypropylene regin (a) / hydrogenation block-copolymer (b) =10 / 90 - 90/10 (weight ratio).

[0007] A well-known thing can be used as a polypropylene regin (a) which constitutes the resin constituent of this invention, and you may be any of gay polypropylene, random polypropylene, and block polypropylene. Moreover, a polypropylene regin (a) may be used independently and may use two or more sorts together. As for the melt viscosity of a polypropylene regin (a), it is

desirable that the melt flow rate (MFR) when measuring in 230 degrees C and 2160g of loads according to ASTMD-1238 is within the limits of 0.1-500, and it is more desirable that it is within the limits of 2-200.

[0008] On the other hand, the hydrogenation block copolymer (b) which constitutes the resin constituent of this invention The polymer block A which consists of a vinyl aromatic compound One or more pieces, (b-1) And the content (the content of 1 and 2-combination and 3 and 4-combination may be hereafter called a vinyl joint content for short) of 1 and 2-combination and 3 and 4-combination has one or more 10-75-mol blocks [ polyisoprene ] B it is [ blocks ] %. The hydrogenation block copolymer which the content of a vinyl aromatic compound is 10 - 40 % of the weight, and comes to hydrogenate 70% or more of the carbon-carbon double bond of the polyisoprene block B, The polymer block A which consists of a vinyl aromatic compound At least one or more pieces, (b-2) And it consists of a polymer of the mixture which comes to mix an isoprene and a butadiene by the weight ratio of 5 / 95 - 95/5. A vinyl joint content has one or more 20-85-mol blocks [ polymer ] C it is [ blocks ] %. The hydrogenation block copolymer which the content of a vinyl aromatic compound is 10 - 40 % of the weight, and comes to hydrogenate 70% or more of the carbon-carbon double bond of the polymer block C, The polymer block A which consists of a vinyl aromatic compound And (b-3) at least one or more pieces, And it has one or more polybutadiene blocks D whose contents of 1 and 2-combination are more than 45 mol %. The content of a vinyl aromatic compound is 10 - 40 % of the weight, and they are at least one sort of polymers chosen from the group which consists of a hydrogenation block copolymer which comes to hydrogenate 70% or more of the carbon-carbon double bond of the polybutadiene block D.

[0009] These hydrogenation block copolymers (b-1) and (b-2) (b-3) the polymer block A which can be set consist of vinyl aromatic compounds. As this vinyl aromatic compound, although styrene, an alpha methyl styrene, 1-vinyl naphthalene, 3-methyl styrene, 4-propyl styrene, 4-cyclohexyl styrene, 4-dodecyl styrene, 2-ethyl-4-benzyl styrene, 4-(phenyl butyl) styrene, etc. are mentioned for example, styrene is desirable also in these.

[0010] Although especially the number average molecular weight of the polymer block A is not restricted, it is desirable that it is within the limits of 2,500-20,000.

[0011] moreover, the content of the vinyl aromatic compound polymer in a hydrogenation block copolymer (b) -- (b-1) -- and (b-2) (b-3) needs to be in 10 - 40% of the weight of within the limits also in which polymer When the content of the vinyl aromatic compound polymer in a hydrogenation block copolymer (b) is less than 10 % of the weight, the mechanical strength of a hydrogenation block copolymer (b) becomes inadequate. Moreover, if the content of the vinyl aromatic compound polymer in a hydrogenation block copolymer (b) exceeds 40 % of the weight, the melt viscosity of a hydrogenation block copolymer (b) will become remarkably high, and since mixing with a polypropylene regin (a) uniformly becomes difficult, the restrictions on a fabricating operation are received.

[0012] It is required for the polyisoprene block B which constitutes a hydrogenation block copolymer (b-1) to have a vinyl joint content in the 10-75-mol range of %, and to hydrogenate 70% or more of the carbon-carbon double bond. The transparency of the moldings obtained from a resin constituent when the vinyl joint content in the polyisoprene block B is less than [ 10 mol % ] is not enough, and when the vinyl joint content in the polyisoprene block B exceeds 75-mol %, the glass transition temperature (Tg) of the polymer block B becomes high too much, and the flexibility of the moldings obtained from a resin constituent is spoiled.

[0013] Moreover, when the rate of hydrogenation of the carbon-carbon double bond of the polyisoprene block B is less than 70%, a hydrogenation block copolymer (b-1) is inferior in compatibility with a polypropylene regin (a), and the transparency of the moldings obtained from a resin constituent is spoiled.

[0014] Although especially the number average molecular weight of the polyisoprene block B is not restricted, it is desirable that it is within the limits of 10,000-200,000.

[0015] Moreover, it is required for the polymer block C in a hydrogenation block copolymer (b-2) to consist of mixture which comes to mix an isoprene and a butadiene by the weight ratio of 5 / 95 - 95/5, and for a vinyl joint content to be in the 20-85-mol range of %, and to hydrogenate 70% or more of the carbon-carbon double bond moreover.

[0016] In the mixture of the isoprene which constitutes the polymer block C, and a butadiene, if the content of an isoprene exceeds 95 % of the weight, the flexibility of a moldings in which the polymer block C is acquired from a resin constituent by (Tg) becoming [ the glass transition temperature ] high too much when a vinyl joint content becomes more than 75 mol % will be spoiled. On the other hand, since the transparency of the moldings obtained from a resin constituent falls when the content of an isoprene is less than 5 % of the weight in the mixture of an isoprene and a butadiene, and the vinyl joint content of the polymer block C becomes less than [ 30 mol % ], it is not desirable.

[0017] Moreover, the transparency of the moldings obtained from a resin constituent when the vinyl joint content in the polymer block C is less than [ 20 mol % ] is not enough, and when the vinyl joint content in the polymer block C exceeds 85-mol %, the glass transition temperature (Tg) of the polymer block C becomes high too much, and the flexibility of the moldings obtained from a resin constituent is spoiled.

[0018] When the rate of hydrogenation of the carbon-carbon double bond of the polymer block C is less than 70%, a hydrogenation block copolymer (b-2) is inferior in compatibility with a polypropylene regin (a), and the transparency of the moldings obtained from a resin constituent is spoiled.

[0019] Especially the polymerization gestalt of an isoprene and a butadiene in the polymer block C may not have a limit, and randomness, a block, tapered one, etc. may be which gestalten. Moreover, although especially the number average molecular weight of the polymer block C is not restricted, it is desirable that it is within the limits of 10,000-200,000.

[0020] Moreover, a vinyl joint content is more than 45 mol %, and the polybutadiene block D in a hydrogenation block copolymer (b-3) needs to hydrogenate 70% or more of the carbon-carbon double bond. When the vinyl joint content in the polybutadiene block D is less than [ 45 mol % ], the transparency of the moldings obtained from a resin constituent is not enough.

[0021] Moreover, when the rate of hydrogenation of the carbon-carbon double bond of the polybutadiene block D is less than 70%, a hydrogenation block copolymer (b-3) is inferior in compatibility with a polypropylene regin (a), and the transparency of the moldings obtained from a resin constituent is spoiled.
[0022] Especially a limit may not be in the joint format of each polymer block in a hydrogenation block copolymer (b), and you may be a line, the letters of branching, or such arbitrary combination. if the example of the molecular structure in front of the hydrogenation of a hydrogenation block copolymer (b) is shown -- A-(B-A) n, n (A-B), A-(C-A) n, n (A-C), A-(D-A) n, and n (A-D) (here) A expresses the polymer block A, B, C, and D express the polyisoprene block B, the polymer block C, and the polybutadiene block D, respectively, and n is one or more integers. Moreover, you may be the star type (for example, m expresses two or more integers and X expresses the residue of a coupling agent m X (A-B) and here) with which the molecular structure in front of the hydrogenation of a hydrogenation block copolymer (b) made the coupling agent the divinylbenzene, the tin compound, or the silane compound.
[0023] what has various kinds of above-mentioned molecular structures as a hydrogenation block copolymer (b) -- independent -- you may use it -- moreover -- for example, a triblock type thing and a jib -- you may use together two or more sorts of things of the different molecular structure like the mixture of a locked type thing As for the number average molecular weight of this hydrogenation block copolymer (b), it is desirable that it is within the limits of 30,000-300,000.
[0024] The method of hydrogenating the block copolymer which can use a method better known than before as the manufacture method of a hydrogenation block copolymer (b), for example, is obtained by the method of a following (b) - a (c) etc. is mentioned.
(b) The method of carrying out successive polymerization of a conjugated-diene compound and the vinyl aromatic compound, after carrying out the polymerization of the vinyl aromatic compound by making an alkyl-lithium compound into an initiator.
(b) A vinyl aromatic compound, the method of carrying out the polymerization of the conjugated-diene compound continuously, and carrying out distributor shaft coupling of the obtained block copolymer using a coupling agent.
(c) The method of carrying out successive polymerization of the vinyl aromatic compound, after carrying out the polymerization of the conjugated-diene compound by making a dilithium compound into an initiator.
[0025] In the above-mentioned method, although the compound whose carbon numbers of an alkyl group are 1-10 is used as an alkyl-lithium compound, a methyl lithium, an ethyl lithium, a pentyl lithium, n-butyl lithium, s-butyl lithium, and t-butyl lithium are desirable especially. Moreover, as a coupling agent, ester compound; divinylbenzenes, such as halogenated compound; benzoic-acid phenyls, such as a dichloromethane, a dibromomethane, a dichloroethane, a dibromoethane, a dibromobenzene, and a tin tetrachloride, and ethyl acetate, various silane compounds, etc. are mentioned, for example. Furthermore as a dilithium compound, naphthalene dilithium, dilithio hexyl benzene, etc. are mentioned, for example.
[0026] It is used to all the monomer 100 weight sections usually used for a polymerization although the amount of the above-mentioned initiator or the coupling agent used is suitably determined according to the molecular weight of the block copolymer considered as a request within limits from which an initiator serves as the 0.01 - 0.2 weight section, and a coupling agent serves as the 0.04 - 0.8 weight section.
[0027] Moreover, the vinyl joint content in the polyisoprene block B, the polymer block C, and the polybutadiene block D (these may be hereafter called a conjugated-diene block for short) is controllable by using a Lewis base as a cocatalyst in the case of a polymerization. this -- a Lewis base -- ****** -- for example -- a wood ether -- diethylether -- a tetrahydrofuran -- etc. etc. -- ether --; -- ethylene glycol -- a wood ether -- a diethylene glycol -- a wood ether -- etc. etc. -- a glycol ether -- a kind --; -- a triethylamine -- N -- N -- N -- ' -- N -- ' -- - -- a tetramethylethylenediamine (this is hereafter called TMEDA for short) -- N -- - -- a methyl -- a morpholine -- etc. etc. -- an amine -- a system -- a compound -- etc. etc. -- mentioning The amount of the Lewis base used is an amount within the limits used as 0.1-1000 mols per one mol of lithium atoms in a polymerization initiator.
[0028] In the case of a polymerization, an inactive organic solvent is used as a solvent to a polymerization initiator. As this solvent, it is desirable that carbon numbers, such as a hexane and a heptane, use aromatic hydrocarbons [, such as alicycle group hydrocarbon; benzene, ], such as an aliphatic hydrocarbon; cyclohexane of 6-12 and a methylcyclohexane.
[0029] A polymerization is usually performed by the 0-80-degree C temperature requirement, even when based on which polymerization method of the above-mentioned (b) - a (c). Reaction time is usually 0.5 - 50 hours.
[0030] Next, let the block copolymer obtained by the above-mentioned method be a hydrogenation block copolymer (b) by the method that the method to which the hydrogen of a molecule state is made to react using a well-known hydrogenation catalyst in the state where it dissolved in the solvent inactive for a reaction is well-known. As a hydrogenation catalyst used here, it is a Raney nickel catalyst ;P t, Pd, The heterogeneous catalyst which made support, such as carbon, an alumina, and diatomite, support metals; such as Ru, Rh, and nickel; Nickel, the [, such as cobalt, ] -- the organometallic compound which consists of a VIII group's metal, and a triethylaluminum -- The catalyst of a Ziegler type which consists of combination, such as organic alkylaluminum compounds, such as triisobutylaluminum, or an organic lithium compound; Titanium, The metallocene system catalyst which consists of combination of organometallic compounds, such as the screw (cyclopentadienyl) compound of transition metals, such as a zirconium and a hafnium, a lithium, sodium, a potassium, aluminum, zinc, or magnesium, is used. Hydrogenation is usually performed by within the limits ordinary-pressure - 200 kg/cm2 and whose reaction temperature hydrogen pressure is ordinary temperature -250 degrees C. Reaction time is usually 0.1 - 100 hours. The hydrogenation block copolymer (b) obtained by hydrogenation is acquired heating or by carrying out reduced pressure drying, after making (i) reaction mixed liquor solidify with a methanol etc. and performing heating or the so-called steam stripping which is made to carry out reduced pressure drying, or pours out (ii) reaction mixture into a boiling water, is made to carry out azeotropy of the solvent, and is removed.

[0031] The blending ratio of coal of the polypropylene regin (a) in the resin constituent of this invention and a hydrogenation block copolymer (b) is within the limits of polypropylene regin (a) / hydrogenation block-copolymer (b) =10 / 90 - 90/10 (weight ratio). When there are few rates of a polypropylene regin (a) than the above-mentioned range and the mechanical strength of the moldings obtained from a resin constituent becomes inadequate, blood conformity also falls. On the other hand, if the rate of a polypropylene regin (a) exceeds the above-mentioned range, both the flexibility and transparency of a moldings that are acquired from a resin constituent will fall. As for the blending ratio of coal of a polypropylene regin (a) and a hydrogenation block copolymer (b), it is desirable that it is 20 / 80 - 80/20 (weight ratio), and it is more desirable that it is 50 / 50 - 80/20 (weight ratio).
[0032] The resin constituent of this invention can add various additives, such as an antioxidant, an ultraviolet ray absorbent, a light stabilizer, a coloring agent, and a crystalline-nucleus agent, within limits which do not spoil the performance. The amount of these additives used is usually the range of 0.01 - 5 weight section to the thing 100 weight section which totaled the polypropylene regin (a) and the hydrogenation block copolymer (b). Moreover, the resin constituent of this invention can also add tackifiers, such as an aliphatic system resin which consists of a hydrogenation system resin, an olefin, and diolefin polymers, such as hydrogenation coumarone-indene resin, a hydrogenation rosin system resin, a hydrogenation terpene resin, and an alicycle group system hydrogenation petroleum resin. The amount of these tackifiers used is a range which becomes below the 200 weight sections to the thing 100 weight section which totaled the polypropylene regin (a) and the hydrogenation block copolymer (b).
[0033] Moreover, if the resin constituent of this invention is within the limits which does not spoil the meaning of invention For example, a hydrogenation polyisoprene, a hydrogenation polybutadiene, a hydrogenation styrene-butadiene random copolymer, A hydrogenation styrene-isoprene random copolymer, isobutylene isoprene rubber, a polyisobutylene, A polybutene, ethylene-propylene system rubber, polyethylene, and ethylene-alpha olefin copolymer, Other polymer, such as an ethylene vinylacetate copolymer, an ethylene-methacrylic-acid copolymer, ethylene-acrylic-acid copolymers or these ionomers, an ethylene-ethyl-acrylate copolymer, and atactic polypropylene, can be blended. Moreover, the resin constituent of this invention can also be used by request, constructing a bridge by the usual bridge formation method of having used the peroxide etc.
[0034] The resin constituent of this invention can be prepared using kneading machines, such as a single screw extruder, a twin screw extruder, a kneader, a Banbury mixer, and a roll.
[0035] Thus, the obtained resin constituent can be fabricated to a film, sheet, fibrous moldings, and tube-like moldings etc. by the arbitrary fabricating methods, such as injection molding, blow molding, press forming, extrusion molding, and calender fabrication.
[0036] The resin constituent of this invention gives the moldings excellent in transparency while it is excellent in flexibility. Especially, the Hayes (Haze) value is 20 or less, and transparency is very excellent, when it is made into a sheet with a thickness of 1mm. Moreover, the resin constituent of this invention gives moldingses with enough thermal resistance. For this reason, the medical supply manufactured using the resin constituent of this invention is equal to autoclave sterilization, and does not have a problem accompanying Remains ethylene oxide gas. In addition, the medical supply manufactured using the resin constituent of this invention can also apply sterilization, such as gamma ray sterilization. Furthermore, the resin constituent of this invention gives a moldings with good biocompatibility. For example, when the catheter which consists of a resin constituent of this invention is detained for one week in a vein, there is little coating weight to this catheter of constituents of blood, such as a platelet and a fibrin, compared with the conventional catheter which consists of an elasticity vinyl chloride or polyurethane, and there is almost no possibility of generating of a thrombus.
[0037] The resin constituent of this invention is used for medical supplies, such as clothes for a hygienic-goods; operation, such as medical supply; sanitary items, such as catheters, such as an in-the-living-body detention type catheter and a balloon catheter, an artificial blood vessel, blood circuits, a syringe, a hemodialysis machine, a constituent-of-blood eliminator, an artificial lung, and wound covering material, and a disposable diaper, and a disposable sheet for hospitals, etc. taking advantage of the above-mentioned property. In these, the resin constituent of this invention is used taking advantage of the outstanding biocompatibility suitable [ a catheter, a blood bag, an artificial blood vessel, blood circuits, a syringe, the hemodialyzer, a constituent-of-blood eliminator, an artificial lung, etc. ] for body fluid and the medical supply used especially as contacts blood. In addition, as for these medical supplies, the portion to which no portions need to be formed from the resin constituent of this invention, and contact body fluid at least should just be formed from the resin constituent of this invention. For example, in KATE 1 above-mentioned Tell or a blood bag, the portion in contact with body fluid may be formed with the resin constituent of this invention, and the portion which does not contact body fluid may be formed by other resins used for medical application, such as an elasticity vinyl chloride and polyurethane. Moreover, the resin constituent of this invention can be used besides the above-mentioned medical-application way in the field as which flexibility and transparency excellent in the packing field etc. are required.
[0038]
[Example] Hereafter, an example explains this invention concretely. In addition, the mechanical strength of the moldings obtained from the styrene content, the number average molecular weight, the vinyl joint content, the rate of hydrogenation, and resin constituent of the polymer in an example, flexibility, transparency, and thermal resistance were measured by the following methods, respectively.
[0039] (Styrene content) It computed from the weight of each monomer component used for the polymerization.
(Number average molecular weight) The number average molecular weight (Mn) of polystyrene conversion was calculated by GPC measurement.
(Vinyl joint content) The block copolymer in front of hydrogenation was dissolved in deuteration chloroform (CDCl3), 1 H-NMR

spectrum was measured, and the vinyl joint content was computed from the size of the peak corresponding to 1 and 2-combination or 3, and 4-combination.
(Rate of hydrogenation) The iodine number of the block copolymer before and behind hydrogenation was measured, and it computed from the measured value.
(Mechanical strength of a moldings) The sheet with a thickness of 1mm was produced, the test piece of the shape of a dumbbell specified to JIS-3 No. from this sheet was pierced, the tension test was performed based on JIS-K6301, and it asked for breaking strength (kg/cm2), and considered as the index of a mechanical strength.
(Flexibility of a moldings) A sheet with a thickness of 1mm is produced and it is ASTM. According to D-2240, the degree of hardness was measured and it considered as the index of flexibility.
(Transparency of a moldings) The sheet with a thickness of 1mm was produced, the Haze value was measured in Haze meter based on the method specified to JIS-K7105, and it considered as the index of transparency.
(Thermal resistance of a moldings) The sheet with a thickness of 1mm was produced, the obtained sheet was left in air at 100 degrees C for 5 hours, the existence of coloring was observed visually, and it considered as the heat-resistant index.
[0040] The examples 1-6 (manufacture of a hydrogenation block copolymer) of reference
Among the proof-pressure container replaced with dry nitrogen, after carrying out the polymerization of the styrene at 60 degrees C, using s-butyl lithium as a polymerization initiator, using a cyclohexane as a solvent, TMEDA was added as a Lewis base, subsequently the polymerization of an isoprene and the styrene was carried out one by one, and the styrene-isoprene-styrene type block copolymer was obtained. It is 20 kg/cm2, using Pd/C as a catalyst by using the obtained block copolymer into the inside of a cyclohexane. Hydrogenation was performed under hydrogen atmosphere and the hydrogenation block copolymer was obtained (the hydrogenation block copolymer obtained in the examples 1-6 of reference is hereafter called for short the hydrogenation block copolymers 1-6, respectively). The styrene content, the number average molecular weight, the vinyl joint content, and the rate of hydrogenation of the obtained hydrogenation block copolymers 1-6 are shown in Table 1.
[0041] The examples 7-12 (manufacture of a hydrogenation block copolymer) of reference
Like the examples 1-6 of reference, the polymerization of the mixture [an isoprene / butadiene =60 / 40 (weight ratio)] and styrene of styrene, an isoprene, and a butadiene is carried out one by one among a cyclohexane solvent using s-butyl lithium and TMEDA, and it is styrene. -(isoprene/butadiene)- The styrene type block copolymer was obtained. The hydrogenation block copolymer was obtained by hydrogenating the obtained block copolymer like the examples 1-6 of reference (the hydrogenation block copolymer obtained in the examples 7-12 of reference is hereafter called for short the hydrogenation block copolymers 7-12, respectively). The styrene content, the number average molecular weight, the vinyl joint content, and the rate of hydrogenation of the obtained hydrogenation block copolymers 7-12 are shown in Table 1.
[0042] The examples 13-17 (manufacture of a hydrogenation block copolymer) of reference
Like the examples 1-6 of reference, using s-butyl lithium and TMEDA, the polymerization of styrene, a butadiene, and the styrene was carried out one by one, and the styrene-styrene-butadiene-rubber type block copolymer was obtained among the cyclohexane solvent. The hydrogenation block copolymer was obtained by hydrogenating the obtained block copolymer like the examples 1-6 of reference (the hydrogenation block copolymer obtained in the examples 13-17 of reference is hereafter called for short the hydrogenation block copolymers 13-17, respectively). The styrene content, the number average molecular weight, the vinyl joint content, and the rate of hydrogenation of the obtained hydrogenation block copolymers 13-17 are shown in Table 1.
[0043]
[Table 1]

表1

| | 水添前の分子構造（注） | スチレン含有量（重量%） | 数平均分子量（x10³） | ビニル結合含有量（モル%） | 水素添加率（%） |
|---|---|---|---|---|---|
| 参考例1 | A－B－A | 20 | 10.3 | 55 | 80 |
| 参考例2 | A－B－A | 20 | 10.6 | 8 | 81 |
| 参考例3 | A－B－A | 20 | 10.5 | 82 | 83 |
| 参考例4 | A－B－A | 20 | 10.2 | 57 | 65 |
| 参考例5 | A－B－A | 8 | 10.8 | 58 | 80 |
| 参考例6 | A－B－A | 45 | 9.8 | 56 | 81 |
| 参考例7 | A－C－A | 20 | 10.8 | 60 | 82 |
| 参考例8 | A－C－A | 20 | 10.2 | 16 | 80 |
| 参考例9 | A－C－A | 20 | 10.6 | 88 | 86 |
| 参考例10 | A－C－A | 20 | 9.6 | 57 | 64 |
| 参考例11 | A－C－A | 8 | 10.5 | 61 | 83 |
| 参考例12 | A－C－A | 45 | 9.6 | 62 | 83 |
| 参考例13 | A－D－A | 20 | 10.5 | 72 | 83 |
| 参考例14 | A－D－A | 20 | 9.8 | 38 | 85 |
| 参考例15 | A－D－A | 20 | 10.2 | 74 | 65 |
| 参考例16 | A－D－A | 8 | 9.7 | 72 | 84 |
| 参考例17 | A－D－A | 45 | 10.3 | 75 | 85 |

（注）A：ポリスチレンブロック
B：ポリイソプレンブロック
C：ポリ（イソプレン／ブタジエン）ブロック
D：ポリブタジエンブロック

[0044] The hydrogenation block copolymers 1-17 which used commercial polypropylene [MA-3 (tradename) and the Mitsubishi Chemical make] as examples 1-3 and the example 1 of comparison - 14 polypropylene regins, and were obtained in the examples 1-17 of reference, and a polypropylene regin / hydrogenation block copolymer = it blended at 70/30 (weight ratio) of a rate, it kneaded at 210 degrees C by the kneader, and the resin constituent was obtained. Press forming of the obtained resin constituent was carried out to the sheet with a thickness of 1mm at 210 degrees C, and a mechanical strength, flexibility, transparency, and heat-resistant measurement were performed. A result is shown in Table 2. Moreover, about the resin constituent obtained in the examples 1-3, blood conformity was evaluated as follows. Consequently, 45 platelet counts /which adhered on the surface of the test piece were [ mm ] 2 (resin constituent obtained in the example 1), 53 piece/mm2, and (resin constituent obtained in the example 2) 60 piece/mm2, respectively (resin constituent obtained in the example 3).

[0045] Press forming of the evaluation resin constituent of blood conformity is carried out to a sheet with a thickness of 1mm at 210 degrees C, the obtained sheet is cut in a 1cmx1cm size, and a test piece is produced. It was immersed in the heparin addition whole blood added and prepared so that might become the Homo sapiens blood after blood collecting about this test piece and it might become 5 IU(s)/ml concentration about the sodium salt of a heparin for 30 minutes at 37 degrees C. After taking out a test piece from a heparin addition whole blood and washing by the physiological saline, by processing a front face using a glutaraldehyde and osmium <8> oxide, by fixing and observing the obtained sample using an electron microscope, it asks for the platelet count which adhered on the surface of the test piece, and considers as the index of blood conformity. Blood conformity is so good that there are few platelet counts which adhered on the surface of the test piece.

[0046] The polypropylene regin of the example of comparison 15 above was used independently, the sheet with a thickness of 1mm was produced like the above, and various kinds of physical properties were measured. A result is collectively shown in Table 2.

[0047]

[Table 2]

表 2

| | 水添ブロック共重合体No. | 破断強度 ($kg/cm^2$) | 透明性 (Haze値) | 柔軟性 (硬度) | 耐熱性 (着色の有無) |
|---|---|---|---|---|---|
| 実施例 1 | 1 | 380 | 18 | 42 | 無 |
| 比較例 1 | 2 | 360 | 65 | 44 | 無 |
| 比較例 2 | 3 | 375 | 25 | 65 | 無 |
| 比較例 3 | 4 | 350 | 47 | 42 | 有 |
| 比較例 4 | 5 | 245 | 24 | 40 | 無 |
| 比較例 5 | 6 | 320 | 67 | 67 | 無 |
| 実施例 2 | 7 | 375 | 21 | 41 | 無 |
| 比較例 6 | 8 | 355 | 63 | 42 | 無 |
| 比較例 7 | 9 | 360 | 30 | 66 | 無 |
| 比較例 8 | 10 | 360 | 43 | 42 | 有 |
| 比較例 9 | 11 | 220 | 25 | 40 | 無 |
| 比較例 10 | 12 | 300 | 65 | 68 | 有 |
| 実施例 3 | 13 | 375 | 23 | 42 | 無 |
| 比較例 11 | 14 | 330 | 66 | 45 | 無 |
| 比較例 12 | 15 | 340 | 62 | 42 | 有 |
| 比較例 13 | 16 | 230 | 28 | 40 | 無 |
| 比較例 14 | 17 | 295 | 62 | 64 | 無 |
| 比較例 15 | — | 455 | 86 | 73 | 無 |

[0048] The hydrogenation block copolymer 1 which used commercial polypropylene [MA-3 (tradename) and the Mitsubishi Chemical make] as an example 4 and 5 polypropylene regins, and was obtained in the example 1 of reference, A polypropylene regin / hydrogenation block copolymer = 80/20 (weight ratio) It blended at a rate of [example 4] or the polypropylene regin / hydrogenation block-copolymer =60/40 [(weight ratio) example 5], it kneaded at 210 degrees C by the kneader, and the resin constituent was obtained. Each of the obtained resin constituent was fabricated on the sheet of thickness lmm like the example 1, and various kinds of physical properties were evaluated. the resin constituent obtained in the example 4 -- breaking strength, flexibility, and transparency -- respectively -- 400 kg/cm2, and 52 (degree of hardness according to ASTM D-2240) and 20 (Haze value) it is -- the platelet count which coloring of a sheet was not accepted but adhered on the surface of the test piece further -- 26 piece/mm2 it was . the resin constituent obtained in the example 5 on the other hand -- breaking strength, flexibility, and transparency -- respectively -- 360 kg/cm2 and 36 (degree of hardness according to ASTM D-2240) And 12 (Haze value) it is -- the platelet count which coloring of a sheet was not accepted but adhered on the surface of the test piece further -- 55 piece/mm2 it was .

[0049] the platelet count which adhered on the surface of the test piece when the test piece which cut and produced the elasticity chlorination vinyl sheet with an example of comparison 16 thickness of 1mm in the 1cmx1cm size was used and blood conformity was evaluated like the above -- 80 piece/mm2 it was .

[0050] The catheter (length : 30cm, an outer diameter : 0.8mm, a bore : 0.6mm) was produced by carrying out extrusion molding of the resin constituent obtained in the six to example 10 examples 1-5 to the shape of a tube. When autoclave sterilization (for 121 degrees C and 20 minutes) was performed to the obtained catheter, it is before and after sterilization processing also about which thing, and change of a configuration and the strong (breaking strength when pulling in the length direction) fall were not accepted. Each of the catheter obtained above was inserted into the rabbit jugular vein, and was detained for seven days. In addition, at this time, the physiological saline was filled inside the catheter and the edge of the direction out of which it has come to the outside of the body from the vein was closed. After taking out the catheter from the rabbit jugular vein and washing by the physiological saline, it fixed by processing a front face with a glutaraldehyde and osmium <8> oxide, and the outside surface of a catheter was observed with the naked eye and the electron microscope. Consequently, 5% of a catheter outside surface (example 6 : catheter obtained from the resin constituent of an example 1) Adhesion of a fibrin and a platelet was observed to 8% (example 7 : catheter obtained from the resin constituent of an example 2), 7% (example 8 : catheter obtained from the resin constituent of an example 3), 4% (example 9 : catheter obtained from the resin constituent of an example 4), and 7% (example 10 : catheter obtained from the resin constituent of an example 5).

[0051] The catheter made from an example of comparison 17 elasticity vinyl chloride (commercial elegance, the Nippon Sherwood Medical Industries make, length:30cm, outer-diameter:0.8mm) was inserted into the rabbit jugular vein like the example 6, and was detained for seven days. After taking out the catheter from the rabbit jugular vein and washing by the physiological saline, it fixed by processing a front face with a glutaraldehyde and osmium <8> oxide, and the outside surface of a catheter was observed with the naked eye and the electron microscope. Consequently, adhesion of a fibrin and a platelet was

observed by about 30% of the outside surface of a catheter.
[0052] The catheter made from example of comparison 18 polyurethane (commercial elegance, the TERUMO CORP. make, length:30cm, outer-diameter:0.8mm) was inserted into the rabbit jugular vein like the example 6, and was detained for seven days. After taking out the catheter from the rabbit jugular vein and washing by the physiological saline, it fixed with a glutaraldehyde and osmium <8> oxide, and the outside surface of a catheter was observed with the naked eye and the electron microscope. Consequently, adhesion of a fibrin and a platelet was observed by about 40% of the outside surface of a catheter.
[0053] By carrying out extrusion molding of the resin constituent obtained in an example 11 and the 12 examples 4 or 5 by the tubular film process, it is a bag. (size : 15cmx 10cm, thickness : 0.5mm) It produced. The platelet strong solution prepared so that the concentration of a platelet might turn into concentration of five units into the obtained bag was put in, and it ****(ed) at the room temperature for 72 hours. When the platelet strong solution was taken out from the bag and the platelet aggregation activity was measured, and it put in into the bag manufactured from which resin constituent and ****(ed), the platelet aggregation activity at the time of collagen addition is 50%, and the condensation ability of a platelet was held good. From this, the bag which consists of a resin constituent obtained in the examples 4 or 5 is understood that blood conformity is good.
[0054] The resin constituent of this invention is excellent in flexibility and transparency, and gives a mechanical strength and moldingses also with enough thermal resistance so that clearly from above-mentioned examples 1-12 and examples 1-18 of comparison. And medical supplies obtained from the resin constituent of this invention, such as a catheter and a blood bag, can perform autoclave sterilization processing, and, moreover, its blood conformity is good also in biocompatibility.
[0055]
[Effect of the Invention] According to this invention, while excelling in flexibility and transparency, the resin constituent which gives the moldings which has sufficient thermal resistance is offered. The resin constituent of this invention is useful in the field as which the outstanding flexibility and outstanding transparency are required, and is suitably used in a medical field especially. Moreover, the resin constituent of this invention is suitable for manufacture of the medical supply especially used also by in biocompatibility as a catheter, a blood bag, an artificial blood vessel, blood circuits, a syringe, the hemodialyzer, a constituent-of-blood eliminator, an artificial lung, etc. contact body fluid since a moldings with good blood conformity is given.

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[Translation done.]

CLAIMS

[Claim(s)]

[Claim 1] The polymer block A which serves as a polypropylene regin (a) from a vinyl (b-1) aromatic compound One or more pieces, And the content of 1 and 2-combination and 3 and 4-combination has one or more 10-75-mol blocks [ polyisoprene ] B it is [ blocks ] %. The hydrogenation block copolymer which the content of a vinyl aromatic compound is 10 - 40 % of the weight, and comes to hydrogenate 70% or more of the carbon-carbon double bond of the polyisoprene block B, The polymer block A which consists of a vinyl aromatic compound One or more pieces, (b-2) And it consists of a polymer of the mixture which comes to mix an isoprene and a butadiene by the weight ratio of 5 / 95 - 95/5. The content of 1 and 2-combination and 3 and 4-combination has one or more 20-85-mol blocks [ polymer ] C it is [ blocks ] %. The hydrogenation block copolymer which the content of a vinyl aromatic compound is 10 - 40 % of the weight, and comes to hydrogenate 70% or more of the carbon-carbon double bond of the polymer block C, The polymer block A which consists of a vinyl aromatic compound And (b-3) one or more pieces, And it has one or more polybutadiene blocks D whose contents of 1 and 2-combination are more than 45 mol %. It consists of at least one sort of hydrogenation block copolymers (b) chosen from the group which consists of a hydrogenation block copolymer which the content of a vinyl aromatic compound is 10 - 40 % of the weight, and comes to hydrogenate 70% or more of the carbon-carbon double bond of the polybutadiene block D. The resin constituent whose rates of both are polypropylene regin (a) / hydrogenation block-copolymer (b) =10 / 90 - 90/10 (weight ratio).

[Claim 2] The medical supply with which the portion which contacts body fluid at least is formed from the resin constituent according to claim 1.

[Claim 3] The medical supply according to claim 2 whose body fluid is blood.

[Claim 4] The medical supply according to claim 2 or 3 which is a catheter, blood circuits, or a blood bag.

[Translation done.]